Precise Size Control in Microgel Synthesis for "Designer Polydispersites"

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Bachelors of Science in Biochemistry

Spring 2013

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Dissertation submitted: Spring 2013

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Acknowledgements:

I would like to acknowledge Dr. L. Andrew Lyon and all other members of this research group for their hard work and help in my project.

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Abstract

The goal of this project was to synthesize a series of monodisperse microgel populations with slightly different average radii. The Lyon group has previously shown that colloidal crystals assembled from hydrogel microparticles (microgels) are extremely tolerant to defects in the form of larger microgel "dopants". To investigate the role of polydispersity in general on crystallization, and to explore the limits of defect tolerance, we have undertaken the synthesis of microgels composed of NIPAM (*N*-isopropylacrylamide) cross linked with BIS (*N,N'*-methylene bisacrylamide) over a range of particle sizes. These dispersions can then be mixed to form dispersions of arbitrary or "designer" polydispersity. These samples will then be analyzed via optical microscopy and neutron scattering in collaboration with the Fernandez-Nieves group.

Summary

Hydrogels have been studied for decades for their numerous unique properties. They can be designed to be responsive to multiple stimuli, such as temperature and pH (1). Hydrogels have been used as possible drug carriers as well. They can also be used to develop and build films, and have been shown to display unique properties that are still being explored. Colloidal dispersions are another avenue that has been explored through the use of hydrogels. Colloidal dispersions have been investigated with respect to the various colloidal phases that form as a function of concentration. The formation of crystals through packing is of particular interest (2). Using soft hydrogels allows for tunable sizes of these particles due to its packing characteristics (3). Using dispersions of multiple monodispersities makes it easier to control the polydispersity of the solution of hydrogels.

Introduction

Nanoparticles are currently being looked at by many scientists as a very versatile tool to be used in many different types of scientific applications, such as drug delivery and use in films. Colloidal crystal packing can be seen in nature when opal gemstones are formed. In this same way, the nanoparticles synthesized from this experiment can be designed to form crystal structures by packing themselves into a compact arrangement. The polydispersity, or range of sizes, of these batches can alter the way in which a crystal is formed by altering how these crystals pack. It is for this reason that these properties must be explored.

Materials/Methods

The goal of this experiment was to create monodisperse series of monodisperse microgel populations with slightly different average radii. Initially, the approach taken to create these monodisperse populations was to alter the total monomer concentration of the two monomers used to synthesize the particles. Another approach was employed in which the concentration of SDS was altered. The synthesis was carried out by using NIPAM (*N*-isopropylacrylamide) cross linked with BIS (*N,N'*-methylene bisacrylamide). The synthesis was stabilized with SDS (sodium dodecyl sulfide) and radical polymerization was initiated with APS (ammonium persulfate). Conditions were kept constant by using a constant stirring speed and water bath temperature.

Figure 1. Set up of the apparatus in which the hydrogels were synthesized.

Results

Using asymmetric flow field flow fractionation (AF4), the monodispersity of some of the samples were analyzed. A 98% NIPAM, 2% BIS synthesis was determined to be about 5% monodisperse (Figure 2).

The radius and polydispersity were measured using dynamic light scattering (DLS) for the syntheses in which the total monomer concentration was changed (Table 1). The radius and polydispersity were measured using DLS for the syntheses in which the total SDS concentration was changed (Table 2).

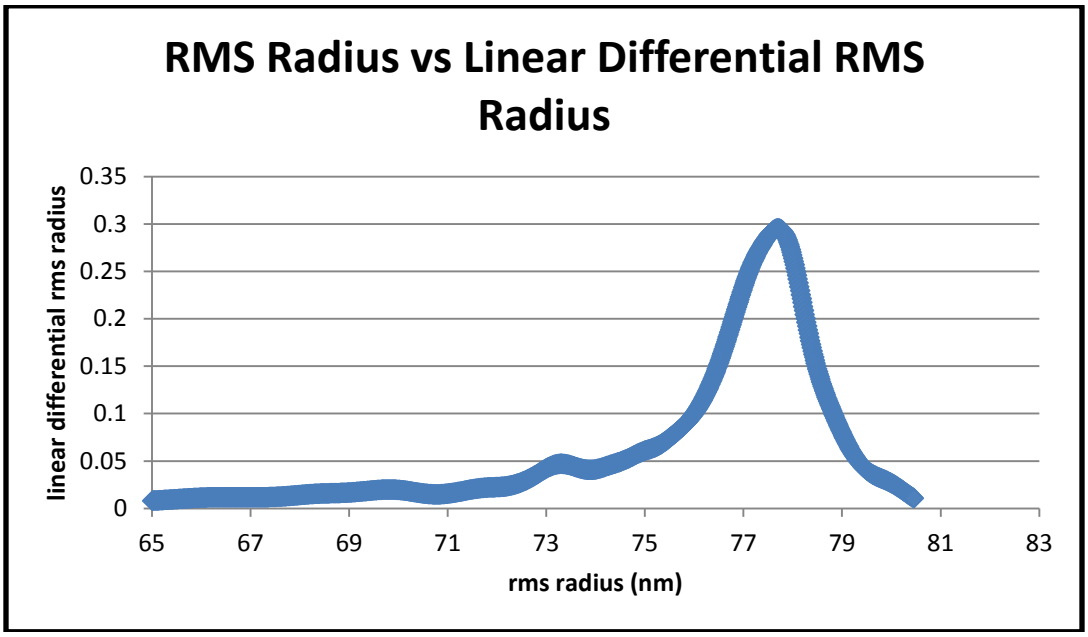

Figure 2. A 98% NIPAM, 2% BIS synthesis analyzed via AF4. The synthesis is about 5% monodisperse.

Table 1. Syntheses with varying total monomer concentration. Data was obtained using DLS.

Synthesis #	Total monomer concentration (mM)	Radius (nm)	polydispersity (nm)
1	50	245 ± 3	46 ± 12
2	70	121 ± 4	31 ± 8
3*	100	132 ± 2	26 ± 8
4*	100	130 ± 0.5	21 ± 3
5	110	134 ± 1	19 ± 4
6	130	130 ± 1	29 ± 6

*all components of synthesis were kept the same with the exception of increased stir speed in Synthesis 4.

Table 2. Syntheses with varying SDS concentration. Data was obtained using DLS.

Synthesis #	SDS Concentration (mM)	Radius (nm)	polydispersity (nm)
3*	1	132 ± 2	26 ± 8
4*	1	130 ± 0.5	21 ± 3
7	2	97 ± 0.5	25 ± 3
8	3	78 ± 0.6	21 ± 3

*all components of synthesis were kept the same with the exception of increased stir speed in Synthesis 4.

Discussion

The batches of particles synthesized during this experiment were initially scaled up from smaller syntheses, which were generally 100 mL in total volume. For this experiment, volumes of 1000 mL were synthesized. Simply scaling up the synthesis and keeping the conditions the same caused some issues and required some troubleshooting in order to attain batches of monodisperse particles. A water bath was used to control the temperature of the synthesis as the hydrogels formed (Figure 1). The apparatus was covered with foil to prevent water from evaporating. The stir speed was also altered to create a more uniform stir speed throughout the synthesis.

Batches of particles of varying monodispersities were successfully created by means of altering SDS concentration. Initially it was thought that varying total monomer concentration could result in varying particle sizes. Six syntheses of five differing total monomer concentrations were conducted and analyzed via DLS (Table 1). Though DLS is a common method of characterizing particles, it is not a very good indicator of polydispersity of these particles, thus AF4 was conducted in order to ascertain a more accurate polydispersity of the particles. Asymmetric flow field flow fractionation (AF4) is a method of fractionation in which particles in a sample are separated due to a cross flow of a carrier solution. A sample injected

into the system is subjected to a parabolic flow that is perpendicular to the direction of the crossflow. This causes the particles to be focused into one area, at which point fractionation can begin and the particles can be separated. Dynamic light scattering (DLS) was used to characterize the particles as well. This method is carried out by subjecting a sample to a laser at 90°. The intensity of the light scattered by the laser is measured as a function of time, and from this, the particles can be characterized. Analysis via DLS showed that particle size did not change significantly with changes in total monomer concentration, especially as the total monomer concentration increased. In order to achieve a considerable change in particle size, change in SDS concentration was introduced while keeping the total monomer concentration constant. Since Syntheses 3 and 4 resulted in highly monodisperse particles (concluded from AF4 analysis), it was decided that the total monomer concentration would be kept at 100 mM and the SDS concentration would be altered. This resulted in a greater change in particle size (Table 2). Increasing SDS concentration resulted in a decrease in particle size. For future work, it would be useful to make larger particles.

From this project, it was determined that altering the SDS concentration seemed to be the most efficient method for creating tunable batches of hydrogel particles. This method resulted in particles that were very monodisperse, and altering the concentration of the SDS resulted in many different sizes of particles as well. Scaling up from a 100 mL synthesis to a 1000 mL synthesis required changes in the apparatus set up and the conditions in which the synthesis was carried out. For the future, it would be beneficial to have a more controlled water bath in which the particles can be synthesized.

References

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